

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Refractory Coating Compositions.

We, NALCO CHEMICAL COMPANY, a Corporation organized under the laws of the State of Delaware, United States of America, of 180 North Michigan Avenue, Chicago, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a refractory coating composition comprising refractory particles suspended in an aqueous binder and process for forming a protective refractory coating on a solid surface.

The refractory coatings referred to in the subject invention are in the form of slurries having a viscosity which is less than 1,000 cps. prior to the addition of suspending agents. The slurries are used for a variety of applications in which they are applied to solid surfaces and dried to form a dense, tightly adherent, refractory coating in a thickness of $\frac{1}{2}$ inch or less.

Refractory coatings have been found to be useful in a number of applications, where a coated surface with a desired characteristic such as absorption, heat reflectivity, slag resistance or resistance to other chemical reaction, resistance to wear and abrasion, resistance to penetration by molten metal and various other special characteristics are desirable.

Refractory coatings of various types have been found to be very useful in a number of applications. However, certain problems exist, which are inherent in the handling of a slurry of low viscosity which contains a relatively dense particulate material. Perhaps, the most serious problems encountered in the handling of slurries, such as those referred to above, occurs due to lack of

stability of the slurry. This results in the particulate material settling out of suspension. Lack of stability of refractory coating slurries accounts for difficulty of transporting them in the slurry form. Mixing problems occur at their use site, when they are shipped separately as a dry refractory component and a liquid binder component. Equipment and application problems often happen when particulate material comes out of suspension and clogs lines, hoses, pumps and other equipment used in applying coatings.

It is an object of the subject invention to produce a refractory coating composition which is a stable suspension of refractory particles in an aqueous liquid binder.

Another object of the invention is to provide a process for forming protective refractory coatings on solid surfaces by the application of a coating in the form of a stable suspension.

A specific object of the invention is to provide a process for forming a protective refractory coating on the surface of cast iron stools, which are used in a process of casting steel ingots.

In accordance with the invention, a novel refractory coating composition has been discovered, which is in the form of a stable suspension of refractory particles suspended in an aqueous liquid binder. The stability of the suspension has been achieved by the addition of a stabilizing amount of a material which is generally known as hectorite clay which is included in an amount from 0.1 to 4.0 per cent by weight.

The suspension of the subject invention has stability at low viscosities. Coating compositions of the subject invention have been found to be stable at viscosities of from 300 to 3000 cps. The suspensions have

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been found to be stable even though relatively dense particulate materials have been used, such as fused silica, alumina, quartz, zirconia, mullite, various aluminosilicates and zircon. The suspensions have been stable even though the particulate materials referred to above have been used in particle sizes as coarse as 100 mesh, as measured by the U.S. Standard Sieve Series.

In a preferred embodiment of the invention, where the aqueous binder employed is a colloidal silica sol, the addition of hectorite clay, as the suspension stabilizing agent, has been found to be particularly useful. The particular usefulness of colloidal silica is a result of the fact that the hectorite clay does not cause the formation of an irreversible gel when mixed with silica sols. Most clays and particularly those with good suspending properties, such as most bentonites, are incompatible with colloidal silica sols in that they cause the formation of a permanent gel, which is actually a hydrated solid and is not useful in any way as refractory coating material.

The hectorite clay referred to in the subject invention is an impure saponite containing material which occurs in commercial quantities in a deposit at Hector, California. This material consists of about 50% to 60% of saponite, the rest being mainly calcium carbonate.

The hectorite is most preferably used in a finely pulverized form. Pulverizing is achieved by grinding to reduce the clay to a powder of about 200 mesh or finer, as measured by the U.S. standard sieve series. A coarser material can be used, but it is slower in dispersing and hence slower acting to stabilize the suspension. The hectorite is quite insoluble in water, but appears to go into an oily appearing suspension of apparently water swollen particles. These

particles, which are distributed throughout the water that is undergoing treatment, appear to be endowed with the special properties necessary to stabilize a suspension, which does not deteriorate under high shear mixing.

Typical physical and chemical properties of the hectorite clay which is useful in the subject invention are given in Table I below.

TABLE I

Typical Physical and Chemical Properties

X-ray Analysis

50%	Saponite
40%	Calcite
3%	Dolomite
1%	Quartz

Moisture 7.1%

Screen Analysis (Dry)

99.0%	through 100 mesh
85.6%	through 200 mesh
66.1%	through 325 mesh

Chemical Analysis (Dry Basis)

SiO ₂	37.29%
Al ₂ O ₃	0.10
Fe ₂ O ₃	0.12
MgO	17.04
Na ₂ O	1.65
CaO	20.15
K ₂ O	.08
Li ₂ O	.75
CO ₂	16.24
SO ₂	.03
Cl	.30
H ₂ O (bound)	6.25

In their most general forms, refractory coating compositions of the subject invention comprise the compositions as shown in Table II below.

TABLE II

	General	Preferred	Most Preferred
Refractory particles	30—80	40—70	40—60
Aqueous Binder	20—70	30—60	40—60
Hectorite clay	0.1—4.0	1.0—3.0	2.0—3.0

The refractory is silica, alumina, zirconia or a combination thereof. It is, of course, understood that the silica, alumina, zirconia, or combinations thereof may be in any of a great variety of crystalline forms in which the pure materials or various combinations of these materials occur. The most preferred of the materials, which are combina-

tions of alumina and silica are kyanite, mullite and various calcined aluminosilicate groups. The most preferred material, which is a combination containing zirconia, is zircon.

A most preferred granular refractory for use in the coating composition of the subject invention is vitreous silica. Vitreous

silica is a glassy modification of silica, obtained by the fusion of selected low-temperature crystalline forms and frequently referred to as quartz glass, silica glass or fused silica. Specific vitreous silicas include fused quartz glasses, silicate glasses, silica glasses, such as the well-known Vycor materials and fused silica glasses. With respect to all of these materials, the thermal expansion coefficients are relatively small compared to other refractories. Generally, vitreous silicas have thermal expansion coefficients smaller than 5×10^{-6} m. per m. per degree centigrade. The silica content of these vitreous silica materials is generally greater than 96% silica, expressed as SiO_2 , and may range as high as 99.8% SiO_2 . Therefore, the term "vitreous silica" describes a refractory comprising a silica glass

having a coefficient of expansion and SiO_2 content within the above range.

Aqueous binders which are useful in the subject invention may be solutions of sodium silicate, potassium silicate, soluble phosphates and other similar material or colloidal dispersions of hydrous and metal oxides, such as colloidal silica or alumina-coated silica sols.

The most preferred aqueous binders for use in the subject invention are the colloidal silica sols. Colloidal silica sols are well known materials and are commercially available from several sources. A typical group of commercially available silica sols, which are useful in the subject invention, are those sold under the name "NALCOAG". Silica sols of this type are described below in Table III.

TABLE III							
Silica Sol	I	II	III	IV	V	IV	
Percent colloidal silica as SiO_2	15	30	35—36	31—22	49—50	35	
pH	8.6	10.2	8.6	3.7	9.0	3.5	
Viscosity at 77°F. cps.	Less than 5	Less than 5	Less than 5	Less than 10	20—30	6.5	
Specific Gravity at 68°F.	1.09	1.205	1.255	1.06	1.385	1.255	
Average Surface Area M^2 per gram of SiO_2	330—430	190—270	135—190	135—190	120—150	135—190	
Average Particle size millimicrons	7.9	11—16	16—22	16—22	20—25	16—22	
Density pounds/U.S. gallon at 68°F.	9.1	10.0	10.5	8.8	11.6	10.5	
Na_2O Percent	0.04	0.40	0.10	0.05	0.30	0.01	

Silica sols, which are useful in the subject invention may be prepared by any of several well known techniques. A convenient method of manufacturing silica sols is described in Bird, U.S. Patent 2,244,325 wherein a dilute solution of an alkali metal silicate is passed in contact with a cationic ion exchange resin in hydrogen form, whereby the silicate is converted to a dilute aqueous colloidal silica sol. The dilute sol may be concentrated to solids concentration which are more economically useful by employing the techniques described in either Bechtold et al, U.S. Patent 2,574,902; Broge et al, U.S. Patent 2,680,721 or Alexander et al, U.S. Patent 2,601,235. It must be understood that the subject invention is not limited

to the use of a colloidal silica sol which is prepared by any particular method. For purposes of the subject invention, a colloidal silica sol is defined as any colloidal dispersion of silica particles in water or in a mixture of water and inorganic substances which is compatible with water.

In a particularly preferred embodiment of the subject invention, the colloidal silica particles are dispersed in a mixture of water and an organic substance which lowers the freezing point. These sols are particularly useful during the colder months of the year, when they must be stored and/or used at relatively low temperatures.

Preferred organic materials for use in

lowering the freezing point of colloidal silica sols are amines such as morpholine, diethyl amine, etc. and polyhydroxy organics such as ethylene glycol; propylene glycol 1,2, propylene glycol 1,3, glycerine, etc. A preferred sol, which is winterized against freezing contains 5—50 parts by weight of a polyhydroxy compound such as ethylene glycol, 20—85 parts by weight of water and 10—60 parts by weight of silica.

It is desirable that the sols for use in the subject invention contain silica particles which are dense, amorphous and have an average particle diameter which does not exceed 150 millimicrons. Preferably, the silica sols should have an average particle size diameter of from 3—60 millimicrons. The silica concentration in the sols may be between 0.1% and 60% by weight silica, expressed as SiO_2 . More preferred sols contain from 3.0 and 60% by weight of silica and most preferably, 10.0 and 60% by weight. These sols are further characterized as having specific surface areas of at least 20 m^2/g and usually in excess of 100 m^2/g .

The invention will be better understood with reference to the following examples.

EXAMPLE I

A slurry was prepared by mixing approximately equal parts by weight of minus 100 mesh fused silica and a colloidal silica sol corresponding to sol #2 from Table III. 2.0 Parts by weight of Hectorite, based on the weight of the slurry, were added. The mixture was prepared by vigorous mixing with a propeller type mixer. The viscosity of the slurry was found to be approximately 1000 cps.

The resultant slurry remained in suspension very well without mixing and did not deteriorate under conditions of high shear mixing. The slurry was further characterized as being pumpable and capable of being sprayed in fine droplets.

EXAMPLE II

A second slurry was made by the same method of preparation as used in Example I. However, 3.0 parts by weight of Hectorite were added, based on the total weight of the slurry.

This mixture had a viscosity of approximately 2000 cps and demonstrated the same desirable properties as to sheer stability, pumping and spraying characteristics as did the slurry of Example I.

EXAMPLE III

A slurry which was prepared by the method of Example II, was applied to the surface of a series of cast iron stools for use in the manufacture of steel ingots. The slurry was applied under pressure through a nozzle which sprayed the slurry

onto the surface of the stool in the form of fine droplets. The slurry was allowed to dry, forming a dense, tightly adherent, refractory coating on the surface of the stool. The coating had a thickness of approximately 1/16 of an inch.

The coated stool was used to form the bottom of a mold for casting a steel ingot. A steel ingot was cast in the mold and allowed to solidify. After removing the ingot from the stool, it was found that the coating was largely intact and had protected the surface of the stool from penetration or attack by the molten steel.

EXAMPLE IV

A coating was made up in the same manner as the coating of Example II, except that minus 325 mesh calcined alumina was substituted for the fused silica. This coating was applied to the surface of a ladle which was used for transporting molten steel. The coating was dried to form a dense, tightly adherent, refractory layer on the surface of the ladle lining. The ladle was used to transport molten steel which had a certain amount of molten slag floating on its surface. After use, the ladle lining was examined and it was found that the coating had been beneficial in reducing the amount of attack on the lining by the molten slag.

It can be seen from the foregoing examples that the objects of the invention, to produce a refractory coating composition in the form of a stable suspension and to provide a process for forming protective refractory coatings have been substantially achieved.

WHAT WE CLAIM IS:—

1. A refractory coating composition which comprises refractory particles suspended in an aqueous liquid binder, and includes from 0.1 to 4.0 per cent by weight of Hectorite clay.
2. The composition of claim 1 comprising the following:

	Weight %	
Refractory particles ...	30—80	110
Aqueous Binder ...	20—70	
Hectorite Clay ...	0.1—4.0	

3. The composition of claim 1 or 2 in which the refractory comprises at least one silica, alumina, zirconia, or combinations thereof.

4. The composition of claim 3 in which the refractory is vitreous silica.

5. The composition of claim 1, 2, 3 or 4 in which the aqueous binder is an aqueous silica sol.

6. A process for forming a protective, refractory, adherent coating on a solid sur-

face which comprises applying to the surface at least one layer of a coating composition according to any of the preceding claims and vaporizing the liquid phase of the composition to leave a dense, tightly adherent, refractory coating on the surface.

5 7. The process of claim 6 in which the solid surface is a cast iron stool for use in a process of casting steel ingots.

10 8. A refractory coating composition according to claim 1, substantially as described herein.

9. A process for forming a protective, refractory, adherent coating on a solid surface according to claim 6, substantially as 15 described herein.

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